$p(2 \times 2)$ Phase of Buckled Dimers of Si(100) Observed on n-Type Substrates below 40 K by Scanning Tunneling Microscopy

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We have investigated the basic surface reconstruction of Si(100) on well defined surfaces fabricated on various substrates at low temperatures (− 80 K) by scanning tunneling microscopy. Below 40 K, the single $p(2 \times 2)$ phase, a phase never observed before, was observed exclusively on n-type substrates doped in the range of 0.002 to 0.017 Ω cm. We also exclude the possibility of the (2×1) symmetric dimer commonly observed at low temperature (− 10 K) being the basic surface reconstruction by showing that a buckled dimer can be flip-flopped by the tunneling tip.

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The surface reconstruction of Si(100) continues to be a long lasting source of controversy [1–19]. In the history, three possible phases have been considered as the ground state. They are the (2×1) phase composed from symmetric dimers, and the $c(4 \times 2)$ and $p(2 \times 2)$ phases that consist of buckled dimers arranged in an antiferromagnetic and ferromagnetic ordering, respectively. Understanding regarding the ground state of Si(100) has been cultivated much by low temperature scanning tunneling microscopy (LT-STM) experiments [3–12]. The first LT-STM observation of the Si(100) surface at 144 K unambiguously showed buckled dimers arranged in a $c(4 \times 2)$ phase, different from the (2×1) symmetric dimers observed at room temperature [3]. This observation led to the general understandings of the surface accepted these days: (1) the $c(4 \times 2)$ phase is the ground state and (2) the (2×1) symmetric dimers appear at room temperature as a result of a flip-flop motion of buckled dimers.

This picture is now challenged by recent STM experiments carried out at very low temperatures (~ 10 K) [7–9]. At 6 K, Shigekawa *et al.* [7] have observed an emergence and a coexistence of the $c(4 \times 2)$ and $p(2 \times 2)$ phases. On the other hand, two groups [8,9] have reported a reemergence of the (2×1) symmetric dimers at 10 K and interpreted the result differently. Yokoyama and Takayanagi [8] argued that the reemergence of the (2×1) symmetric dimers is due to an anomalous flip-flop motion. In contrast, Kondo *et al.* [9] claimed that the (2×1) symmetric dimers at 10 K are static and posed a question regarding the ground state.

This work is motivated to solve the above conflict and to reconstruct a new general standard understanding of the surface structure of Si(100). We investigated the surface reconstruction of a variety of Si(100) substrates different in types (n and p, specifically), dopants, step densities, and conductivities by voltage dependent STM imaging and tunneling spectroscopy at a wide range of temperatures (9–80 K). In addition, we utilized the recent progress to make a well defined surface with small defect densities [10], a point that was crucial to rule out the influence of defects and access to the intrinsic properties of the surface structure. Central to the results obtained is the observation of a $p(2 \times 2)$ phase, a surface reconstruction that has never been observed before. The $p(2 \times 2)$ phase was observed specifically on n-type substrates doped in a range of (0.002 to 0.017 Ω cm) and not on the p-type substrates we investigated. This result suggests that the Si(100) surface might have a different ground state depending on whether the substrate is doped n or p type. We show that a buckled dimer can be easily flip-flopped by the tunneling tip at low temperature, giving direct evidence that the (2×1) symmetric dimer phase observed at low temperature is not an intrinsic surface phase.

Si(001) samples were ultrasonically cleaned for 10 min in acetone and then loaded into the vacuum chamber and prebaked at ~700 °C for ~5 h with a vacuum pressure below 1.0×10^{-7} Pa. After prebaking, the sample was once flashed to 1200 °C for 10 s to remove the oxidized layers. After the sample and sample holder are completely cooled, an additional flashing was carried out at 1200 °C for a very short time (~ 5 s) to reduce the defect density lower than 1% [10]. After flashing, the sample was transferred to the STM and stable scanning at 9 K could be carried out within 2 h after flashing. The surface remained fairly clean for more than 24 h.

An STM image at 9 K of a wide and perfect $p(2 \times 2)$ phase formed in the middle of a defect-free domain located far away from steps is shown in Fig. 1(a). Several important comments can be made about the observed $p(2 \times 2)$ phase. First, and most importantly, the $p(2 \times 2)$ phase was observed only on n-type substrates. As listed in Table I, we observed the $p(2 \times 2)$ phase on a wide range of n-type substrates different in dopant elements and dopant densities, though the $p(2 \times 2)$ phase was never observed on any of the p-type substrates we studied. Second, the $p(2 \times 2)$ phase was observed only at temperatures below 40 K. A phase transition occurred at around 40 K [Fig. 1(b)] and the surface structure gradually converted to the $c(4 \times 2)$ phase as the temperature raised [Fig. 1(c)]. Third, the $p(2 \times 2)$ phase is not caused by defect and

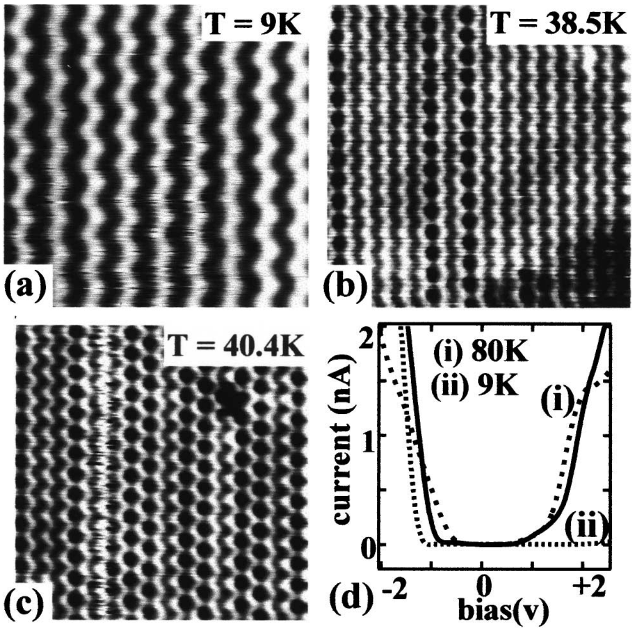

FIG. 1. Observation of the $p(2 \times 2)$ phase. (a) An STM image (7×7 nm) of a $p(2 \times 2)$ domain at 9 K (substrate 2 in Table I). Imaging conditions: $V_s = +1.0$ V; $I_t = 0.4$ nA. (b),(c) STM images (12×12 nm) at 38.5 and 40.4 K, showing the $p(2 \times 2)$-$c(4 \times 2)$ phase transition. Imaging conditions: $V_s = +1.0$ V; $I_t = 0.4$ nA. (d) Tunneling I-V curves. Dotted lines (i) and (ii): I-V curves from substrate 3 in Table I at 80 and 9 K, respectively. Real line: I-V from substrate 2 in Table I at 9 K.

steps. In fact, dimers adjacent to steps and defects had a strong tendency to align in a $c(4 \times 2)$ phase. Wide $p(2 \times 2)$ domains were observed only on surfaces with low defect densities. In contrast, on surfaces with high defect and step densities (substrate 1 in Table I), the surface structure was a mixture of both the $p(2 \times 2)$ and $c(4 \times 2)$ phases [7]. These experimental results suggest that the emergence of the $p(2 \times 2)$ phase is an intrinsic property of n-type substrates and is not caused by defects or subsidiary effects such as decrease of the conductivity of the substrate at low temperatures.

The $p(2 \times 2)$ phase was not observed previously because of two effects: (1) decrease of the conductivity of the substrate at low temperatures and (2) an intriguing dependence of the apparent surface structure observed by STM on bias voltage. Figure 1(d) shows the temperature dependence of the tunneling I-V spectra of an n-type Si(100) substrate (substrate 3 in Table I) that has a dopant density ($\rho = 0.012\ \Omega\,\mathrm{cm}$) typically used for low temperature STM studies. At 80 K, the I-V spectrum showed similar conductivity at both negative (filled state) and positive (empty state) surface biases. At 9 K, the conductivity at positive bias has decreased dramatically, and no tunneling current was measured at typical positive biases used in STM. A similar tunneling rectifying behavior has been observed at room temperature on lowly doped substrates ($\rho = 10\ \Omega\,\mathrm{cm}$) [13]. Thus, the rectifying behavior observed at low temperatures is caused by a suppression of ionization of dopants that leads to a thicker depletion layer beneath the surface that hinders tunneling of electrons ejected from the tip [14].

TABLE I. Substrates we studied the surface phase listed with the resistivity, dopant, types, and the phase observed by STM.

No.	Type	Resistivity (Ω cm)	Dopant	Surface phase
1	n	0.002	As	$p(2 \times 2)$
2	n	0.004	As	$p(2 \times 2)$
3	n	0.012	P	$p(2 \times 2)$
4	n	0.014	Sb	$p(2 \times 2)$
5	p	0.001–0.01	B	⋯
6	p	0.017	B	⋯
7	p	2	B	$c(4 \times 2)$
8	p	4	B	$c(4 \times 2)$

This rectifying behavior poses severe restrictions on STM observations. Since no tunneling current flows at positive biases, empty state imaging is not possible. Inaccessibility to the empty states at very low temperatures explains why the $p(2 \times 2)$ phase has not been observed previously, because the $p(2 \times 2)$ phase was observed by STM only at the empty state as described in the following. We used degenerately doped substrates to image the empty states [note the same results were obtained on other n-type substrates if enough tunneling current could be obtained below 40 K (substrates 2 to 4 in Table I)]. Figure 1(d) shows a tunneling I-V spectrum (real line) at 9 K of an n-type Si(100) substrate (substrate 2 in Table I) that is heavily doped ($\rho = 0.002\ \Omega\,\mathrm{cm}$). A significant tunneling current flows at positive biases enabling empty state imaging. On these substrates, we found an interesting bias dependence of the surface structure by STM observed only below 40 K.

An STM image [Fig. 2(a)] and a scanning tunneling spectroscope (STS) spectrum [Fig. 2(b)] of the surface of an n-type heavily doped substrate (substrate 2 in Table I) at 9 K are presented to show the bias dependence of STM images and the corresponding imaged electronic states [Fig. 2(d)]. The STS spectrum was composed from three main peaks (regions) and was identical to that observed at higher temperatures [2]. Assignment of the three regions was given from recent spatial resolved tunneling spectra studies [15] as (1) the peak in the filled state at -1.0 V to the π filled surface state, (2) the small peak in the empty state at $+0.5$ V to the π^* empty surface state, and (3) tunneling from other states than these two surface states compose the peak at $+1.5$ V. Interestingly, the corresponding STM images of each region were different. First, and most importantly, buckled dimers in a $p(2 \times 2)$ phase were observed when the π^* empty state was probed. Second, apparent (2×1) symmetric dimers were observed at the π filled state. Third, another (2×1) symmetric feature that is out of phase from the dimer rows observed at the other two regions was observed in the empty state high bias region. This (2×1) symmetric

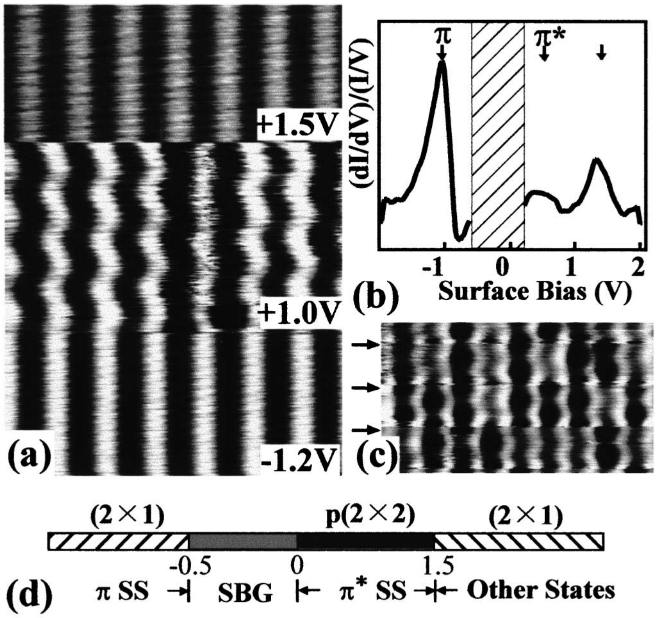

FIG. 2. Surface of n-type substrates. (a) An STM image (5.4×77 nm) of a surface of an n-type substrate at 9 K (substrate 2 in Table I) where the surface bias was changed from -1.2, $+1.0$, and $+1.5$ V. $I_t = 0.4$ nA. (b) Normalized STS spectrum of the same surface at 9 K. Shaded regions represent the surface band gap. (c) An STM image (7×4 nm) at 9 K where the surface bias was changed from positive to negative at locations indexed by arrows. Imaging conditions: $V_s = +1.0$ V; $I_t = 0.4$ nA. (d) A schematic showing the surface phase observed at different biases and the corresponding states for n-type substrates (SSG: surface band gap; SS: surface state).

feature was also observed in all p- and n-type substrates we studied and was also observed at higher temperatures up to room temperature [16,17]. It is established that STM images at this bias region do not reflect the surface structure because tunneling from other states (bulk state and surface resonances) overwhelm tunneling from the π^* surface state [16,17]. If unintentionally this region is observed, one might erroneously conclude that the surface structure is a (2×1) symmetric dimer. This might be one reason of the conflict among researchers regarding the surface phases observed at very low temperatures. The most important issue that has to be clarified is whether the $p(2 \times 2)$ phase or the (2×1) symmetric dimer observed at the filled state reflects the true surface structure. We found direct evidences that indicate the (2×1) symmetric dimers observed at low biases are caused by a flip-flop motion induced by the STM tip. Figure 2(c) shows an empty state STM image of the $p(2 \times 2)$ phase where the scanning was halted at locations indicated by arrows and the bias was switched there from a positive to a negative value. A dramatic change in the surface configuration was observed when the bias was switched. This experimental result is readily explained if a flip-flop motion of the buckled dimers is induced by the tip at negative bias. A more direct evidence of tip induced flip-flop motion was found from experiments on p-type substrates.

STM images of the surface of p-type substrates (substrates 5 to 8 in Table I, doped in the range of 0.002 to 0.017 Ω cm) were very different from images of n-type substrates. First of all, the $p(2 \times 2)$ phase was never observed on all of the investigated p-type substrates at any tunneling conditions. This result is remarkably different from n-type substates where essentially a $p(2 \times 2)$ phase was observed on all of the substrates studied, provided enough tunneling current could be gained for imaging. Instead, on many experimental conditions (on substrates 5 to 8), we observed the (2×1) symmetric dimer. Exceptions were substrates 7 and 8 where a $c(4 \times 2)$ phase, a phase we did not observe on p-type substrates, was observed at least at some bias voltages.

Substrate 8 in Table I showed a very interesting voltage dependence [Fig. 3(a)]. Here, at the very upper edge of the π^* empty state (from $+1.9$ to 2.2 V), the $c(4 \times 2)$ phase was observed. When the voltage was lowered (below $+1.9$ V), even though we were imaging the same π^* empty state, the dimer converted into a (2×1) symmetric configuration. At higher voltages (above $+2.2$ V), the (2×1) symmetric features accompanied with the phase shift were observed, defining the boundary of the π^* surface state. Importantly, at $+1.9$ V, a strong tunneling current dependence was observed: the buckled dimers observed at low current [Fig. 3(b)] gradually transformed into a (2×1) symmetric configuration [Fig. 3(c)] as the tunneling current was increased. Based on an extensive investigation, a phase diagram [Fig. 3(d)] of the phase observed by STM on various tunneling conditions was constructed from which two important points were made clear. First, the $c(4 \times 2)$ phase was observed only in a very narrow window of tunneling conditions and this must have precluded observation of the $c(4 \times 2)$ phase before. Second, the configuration of dimers became symmetric at tunneling conditions where the tip-surface interaction is strong (low bias and high tunneling current). Furthermore, at 80 K, we found that the buckled dimer of the $c(4 \times 2)$ phase could be forced into a symmetric configuration when the tip-surface interaction is extremely strong (tunneling condition: surface bias -1.0 V; tunneling current 60 nA). These observations provide direct evidence that the observed (2×1) symmetric dimers are induced by the tip. Indeed, theoretical calculations predict that a strong tip-dimer interaction would enforce a flip-flop motion giving a (2×1) symmetric configuration in STM images [18].

The appearance of different phases on different substrates or the complicated voltage dependence of the STM image of sample 8 are not readily explained. The experimental results strongly suggest that the conductivity of the substrate is an important factor for the former. We think that the tip-surface interaction is affected by the conductivity of the substrate. Also, we would comment that the surface bias necessary to observe the high bias

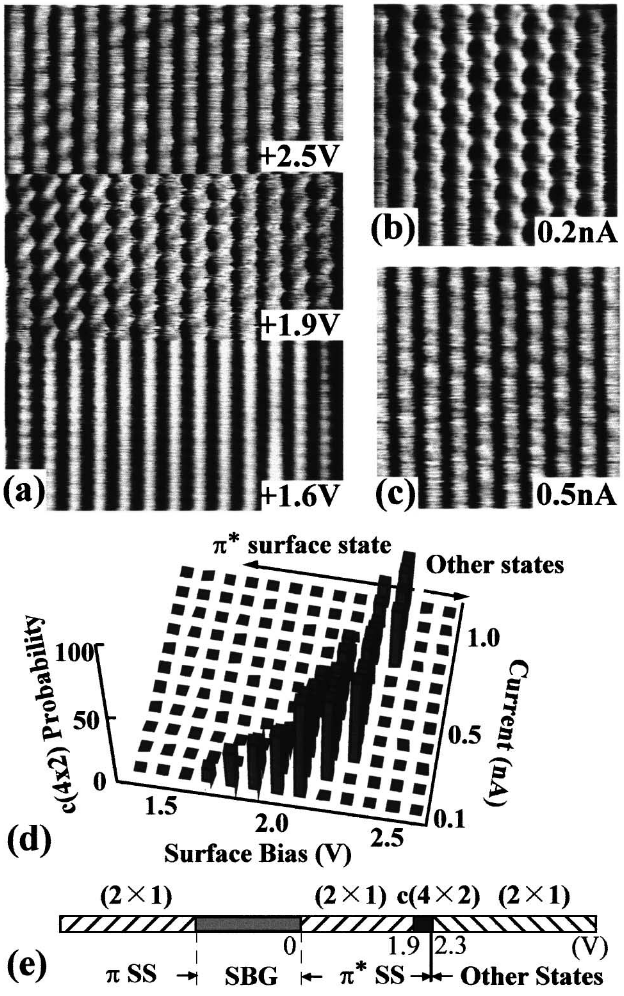

FIG. 3. Surface of p-type substrates. (a) An STM image (10×15 nm) of a surface of a p-type substrate at 9 K (substrate 8 in Table I) where the surface bias was changed from +1.6, +1.9, and +2.5 V. (b),(c) STM images (7×7 nm) at 9 K of the same location with different tunneling currents. $V_s = +1.9$ V. (d) Phase diagram of the existing probability of the $c(4 \times 2)$ phase versus tunneling bias and current. (e) A schematic showing the surface phase observed at different biases and the corresponding states for p-type substrates.

empty state region is higher at sample 8 than in other samples. This means that some voltage drop exists in the depletion layer of sample 8. We speculate that this voltage drop or boron segregation to the surface region [19] might play some role in the specialty of sample 8.

From STM studies alone, it is difficult to understand why the n- and p-type substrates have different surface structures at temperatures below 40 K. First principle calculations predict that the stabilities of the $p(2 \times 2)$ and $c(4 \times 2)$ reconstructions are essentially identical while the (2×1) symmetric dimers are very unstable [20]. Indeed, by STM, at higher temperatures (80–200 K), occasionally a small domain of the $p(2 \times 2)$ phase has been locally observed close to step edges, though their size never spanned more than three or four dimer rows. However, observation of the $p(2 \times 2)$ phase close to the vicinity of the step edges implies that a very small perturbation or difference in environment might change the stable phase. Possible causes we nominate are the existence of the depletion layer beneath the surface and the difference in the Fermi level position between n- and p-type substrates. We hope that our findings further invoke studies to elucidate this interesting issue.

In conclusion, we have implemented a thorough investigation of the surface structure of very clean and well defined Si(100) surfaces at low temperatures below 40 K by STM and STS. The $p(2 \times 2)$ phase, a phase never before observed, was observed specifically on n-type substrates. Since the general belief that the $c(4 \times 2)$ is the ground state of this surface is based on an STM observation of the $c(4 \times 2)$ phase at higher temperatures (80–200 K), our results might give rise to a controversy to the long debated problem: whether the $c(4 \times 2)$ or $p(2 \times 2)$ phase is the ground state of this surface.

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